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Microarticle

Fabrication of cylindrical active GRIN media by laser-assisted radial dopant diffusion: A proof of concept

A.I. Gómez-Varela[a], F. Rey-García[b], I. de Francisco[b], M.T. Flores-Arias[a], G.F. de la Fuente[b], C. Bao-Varela[a,*]

[a] *Unidad Asociada de Microóptica & Óptica GRIN, "Photonics4life" Group, Universidade de Santiago de Compostela, Campus Vida, E-15782 Santiago de Compostela, Spain*

[b] *Instituto de Ciencia de Materiales de Aragón (CSIC), María de Luna 3, E-50018 Zaragoza, Spain*

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ABSTRACT

This work introduces a new approach to prepare active GRadient-INdex (GRIN) materials by gradually doping commercial silica cylindrical substrates with different optically active ions or materials by the Laser Zone Melting (LZM) process. Scanning Electron Microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis demonstrate that the dopants are gradually incorporated into the cylindrical substrate under controlled penetration depths. This simple, environmentally respectful fabrication method opens the possibility to manufacture versatile GRIN optical elements on a large scale and reduced cost.

Introduction

The typical intensity distribution of a laser beam is not always the most suitable one for practical applications. It is possible to transform the irradiance distribution, as well as the phase of a laser beam in a process that is known as beam shaping [1]. It has been previously shown that active GRadient-INdex (GRIN) rod lenses, described by a complex parabolic-like refractive index profile can perform different optical functions such as focusing, collimation and uniform beam shaping [2]. These active GRIN materials are defined as having the capability to amplify or attenuate the irradiance of the beam, depending on whether the optical media exhibits gain or loss. In particular, an input Gaussian beam can be reshaped into one with a uniform irradiance distribution by an active GRIN medium when the beam waist tends to infinite at the output of the material. The predominant fabrication approach of GRIN materials is the ion exchange method, although they can also be obtained by different processes such as Sol-gel, Chemical Vapour Deposition (CVD), molecular stuffing or glass melting [3,4].

Laser Zone Melting (LZM) is a useful method to process ceramics and glass under controlled solidification conditions. It had initially been developed to process functional ceramics under diverse configurations [5,6]. Laser irradiation of a material induces local melting of its surface at the focal spot and its surrounding area and is only limited by the material's melting point and its thermal stability. When combined with directional displacement, it provides a simple method to solidify part of the surface under controlled conditions and an interesting alternative to more conventional synthesis methods. Indeed, Rey-García et al. [6] successfully produced planar step-index waveguides within flat soda-lime glass substrates by this technique, yielding refractive index values of 1.58 and 1.59 for free and Yb-doped lead borosilicate coatings, respectively, as compared to 1.52 for the commercial soda-lime glass. Likewise, they observed an excellent coating-substrate integration and compatibility, favoured by atomic diffusion in the proximity of the interface. Following these principles, this work reports on a proof of concept for fabrication of active radial GRIN materials using the LZM technique. In order to obtain a complex refractive index distribution that varies from the optical axis to the periphery of the material, a CO_2 laser line is focused onto a constantly rotating glass substrate that has been previously coated with the active element. The laser line is oriented orthogonal to the displacement axis so that a stationary surface melt is generated along the outer surface of the cylindrically shaped substrate. The melt uptakes the dopant phase into the volume of the substrate rod, distributing the dopant in a radial fashion within it, via liquid and solid state, high temperature diffusion processes. The approach presented in this investigation is exploratory and implies a single step process where the substrates are directly irradiated by a pulsed CO_2 laser. Substrates were not externally heated simultaneously to laser irradiation in this work, because of the radial geometry and its experimental set-up limitations. For this reason, high irradiance values

* Corresponding author.
E-mail address: carmen.bao@usc.es (C. Bao-Varela).

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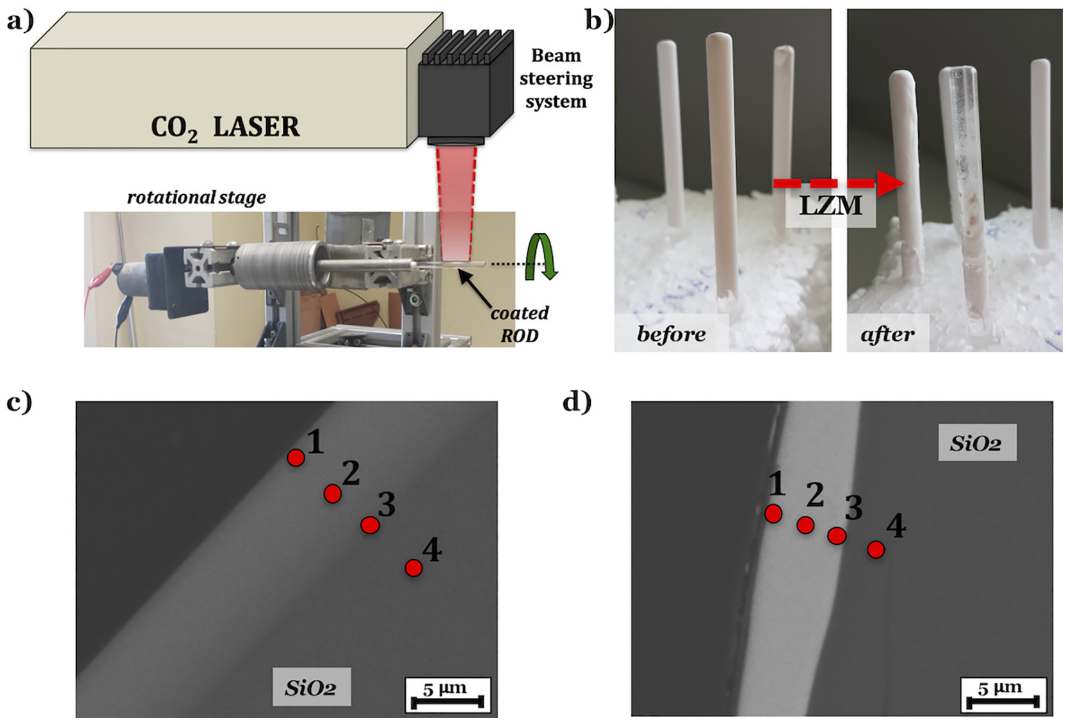

Fig. 1. a) Experimental set-up; b) Photograph of $LiNbO_3$ coated silica rod before and after laser treatment; SEM micrographs of c) $LiNbO_3$ and d) Yb_2O_3 coated SiO_2 rods obtained by applying the conditions reported in the text. Areas for EDX analysis are marked with red dots at coating-top border (1), middle (2) and inner border (3)- and SiO_2 substrate (4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were not employed and SiO_2 was selected as substrate material due to its low thermal expansion, in order to minimize or avoid possible microcracks produced by thermomechanical stress. Rare Earth (RE) and Lithium Niobate (LN) oxides were chosen as doping materials, because their introduction on glass substrates by LZM enabled refractive index modification in planar geometry [6]. Compared to conventional methods, laser processing provides spatially selective, environmentally friendly and scalable treatments which may reduce fabrication costs [7].

Experimental

Isopropyl alcohol suspensions at 60% (in weight) of commercial raw powders of Dy_2O_3 (99.99%), Er_2O_3 (99.99%), Yb_2O_3 (99.99%) and $LiNbO_3$ (99.99%) from MaTeck (Jülich, Germany) were prepared and used to coat commercial 5 mm dia. SiO_2 rods by immersion. Subsequently, the doped rods were processed under a Laser Line Scanning mode [5] by scanning a focused CO_2 laser beam (λ = 10.6 µm, 1100 mm focal distance) onto the surface of the coated rod along its axis at a normal angle. The rods were placed onto a rational stage, as shown schematically in Fig. 1(a) and scanned with a Jeanología Láser (Spain) 350-Marca Flex Model Apparatus fitted with a ROFIN-Sinar 350 W SLAB-type laser emitting in pulsed mode (nominal Laser power 350 W, 50 µs pulse period width, 20 kHz pulse repetition frequency, 23.6 m/s beam scan rate and 6.96 r.p.m. rotation rate). This commercial machine is fitted with a galvanometer mirror unit and adequate software to control laser beam movement with high precision. Morphology and microstructure changes were observed by Field Emission SEM using a Carl Zeiss MERLIN instrument.

Results and discussion

Fig. 1(b) shows the aspect of a representative LN coated silica rod before and after laser treatment under different experimental parameters. Laser induced interaction of the SiO_2 substrate rods with the dip coated LN and RE oxide surface deposits was conveniently assessed by SEM. The consolidation of the coating is easily identifiable as an external layer with a markedly different contrast in the SEM micrographs shown in Fig. 1(c) and (d), for the LN and RE oxide coated rods, respectively. An obvious difference is observed between the diffuse interface in the LN doped sample (Fig. 1c) and the sharp interface in the case of the representative RE doped sample. SEM/EDX analysis of the processed samples revealed chemical adhesion of coatings onto the host material (Fig. 1c and d) with a sharp interface. Furthermore, the dopant phase apparently locates on the outer surface of the rods and appears with a similar cross section to that observed in optical fiber waveguides. In addition, and from the glass waveguide fabrication perspective, the rotation speed applied in the process translates into a traverse solidification rate of 1.82 mm/s, too fast to expect crystallization of the oxide phases introduced into the substrate rod. Consequently, their morphology resembles that of the amorphous SiO_2 rod, well within the desired aim for progressive modification of the refractive index along its radius, avoiding potential unwanted crystallization of complex phases.

Micrographs obtained on LN and RE coated rod samples (Fig. 1c-d) suggest the presence of chemically compatible and continuous coatings along the diameter of the rod. Thus, coatings corresponding to LN doped rods present a uniform layer with thickness above 7 µm and a slightly diffuse interface with the SiO_2 rods. Consequently, a gradual diffusion of dopants should allow the gradual modification of the refractive index of SiO_2, as expected from a previous report [6]. In contrast, equivalent coatings based on rare earth oxides present an irregular thickness, ranging between 3 and 6 µm, and a well-defined, sharp interface, namely a structure resembling that of optical fiber waveguides. Concomitantly, EDX analysis on selected points (Fig. 1c-d) of LN doped sample cross sections shows a gradual decrease of Nb and an increase of Si content from the outer surface of the coating in the radially inward direction. For the RE doped sample, however, the Yb and Si composition is found constant along the coating cross-section (around 15 and 21 at%, respectively). In both cases, the dopant was not

Table 1
EDX analysis performed on $LiNbO_3$ and Yb_2O_3 doped SiO_2 rod samples near their edge, corresponding to areas marked at Fig. 1c) and d), respectively. Values are shown in atomic percentage (at%).

$LiNbO_3$-SiO_2				Yb_2O_3-SiO_2			
Area	Si	Nb	O	Area	Si	Yb	O
(1)	24.07	7.94	67.99	**(1)**	20.72	15.14	64.14
(2)	28.46	4.18	67.36	**(2)**	21.02	14.78	64.20
(3)	32.37	0.83	66.80	**(3)**	20.39	15.53	64.08
(4)	33.33	–	66.67	**(4)**	33.33	–	66.67

detected within the inner core of the substrate (Table 1). The melting points of $LiNbO_3$ (1530 K) and Yb_2O_3 (2650 K) insure conditions for laser promoted atomic diffusion at the coating/substrate interface. The increased diffusion deduced for LN doped SiO_2 rods is consistent with work reported on LN-silica mixtures [8]. Limited diffusion for the Yb coating is consistent with formation of refractory RE silicates at the substrate interface [9]. In any case, LZM enables coupling of both types of materials to silica rods, despite large melt temperature differences. Cracks have been identified along the surface of the processed cylinders, assigned to the exaggerated thermomechanical stress associated to the extreme temperature gradients provoked by narrowly focused laser irradiation [9].

Conclusions

This work presents proof of concept to produce active GRIN materials with cylindrical geometry via the introduction of dopants into commercial silica glass rods using a simple and scalable Laser Zone Melting method. Selective laser melting of coated silica rods with photonic materials such as $LiNbO_3$ and rare earth oxides (Yb_2O_3), shows potential for developing optical elements with controlled dopant distribution along their radius, even when the melt temperatures of the substrate (SiO_2) and the dopant phases ($LiNbO_3$ and Yb_2O_3) are far apart (more than 500 K). A sharp interface was observed by SEM for the Yb_2O_3 coating, yielding a structure resembling that of a waveguide fiber, with the core being pure SiO_2 and the sheath the rare earth oxide. The niobate doped rod exhibited a slightly more diffuse interface, however. These structures suggest the potential of this simple LZM process to develop GRIN optical elements, based on an environmentally respectful and scalable method.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

A.I. Gómez-Varela: Conceptualization, Investigation, Writing - original draft. **F. Rey-García:** Conceptualization, Investigation, Writing - review & editing. **I. de Francisco:** Investigation. **M.T. Flores-Arias:** Investigation, Writing - review & editing. **G.F. de la Fuente:** Supervision, Writing - review & editing. **C. Bao-Varela:** Supervision, Funding acquisition, Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rinp.2020.103142.

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